Solid phase immiscibility in GaInN

I-hsiu Ho and G. B. Stringfellow[a)]
Departments of Material Science and Engineering and Electrical Engineering, University of Utah, Salt Lake City, Utah 84112

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The large difference in interatomic spacing between GaN and InN is found to give rise to a solid phase miscibility gap. The temperature dependence of the binodal and spinodal lines in the $Ga_{1-x}In_xN$ system was calculated using a modified valence-force-field model where the lattice is allowed to relax beyond the first nearest neighbor. The strain energy is found to decrease until approximately the sixth nearest neighbor, but this approximation is suitable only in the dilute limit. Assuming a symmetric, regular-solutionlike composition dependence of the enthalpy of mixing yields an interaction parameter of 5.98 kcal/mole. At a typical growth temperature of 800 °C, the solubility of In in GaN is calculated to be less than 6%. The miscibility gap is expected to represent a significant problem for the epitaxial growth of these alloys. © *1996 American Institute of Physics.* [S0003-6951(96)03944-7]

GaInN alloys have recently attracted much attention as potential materials for the fabrication of blue and green light emitting diodes (LEDs)[1] and violet and blue injection lasers (LDs).[2] Since the band gap energy of GaInN can be varied from 2.0 to 3.5 eV by increasing the GaN concentration,[3] the potential operating wavelengths cover nearly the entire visible spectral range. The optical devices made from GaInN are important for both display and optical data storage applications. The GaN/GaInN system is also potentially important for high temperature and high power electronic devices.[3]

The growth of GaInN alloys has proven to be extremely challenging, mostly due to the trade-off between the epilayer quality and the amount of InN incorporation into the alloy as the growth temperature is changed. Growth using high temperatures of approximately 800 °C typically results in high crystalline quality but the amount of InN in the solid is limited to low values because of the high volatility of N over InN.[4] Matsuoka *et al.*[4] found that by using organometallic vapor-phase epitaxy (OMVPE), lowering the growth temperature from 800 to 500 °C resulted in an increase in the allowable InN concentration range, but at the expense of reduced crystalline quality. Attempts to increase the InN concentration in the solid by raising the In pressure in the vapor results in In droplets on the surface.[5] Some evidence of phase separation was demonstrated in very early (1975) experiments where GaInN samples were annealed in an argon ambient at various temperature below 700 °C.[6] The thermodynamic stability of the GaInN system has not been discussed in detail until now, a somewhat surprising situation in light of the importance of these alloys.

In this letter, a theoretical calculation of the enthalpy of mixing, the solid phase interaction parameter, and the extent of the miscibility gap was performed for the $Ga_{1-x}In_xN$ alloy system using a modified valence-force-field (VFF) model[7] calculation. The VFF model, itself, is found to overestimate the total strain energy of a ternary system due to the constraint that only one of the two sublattices is allowed to relax. For dilute alloys, a modification of the VFF model was made allowing both sublattices to relax, producing a significantly lower enthalpy of mixing. This yields an equilibrium InN mole fraction in GaN at 800 °C of less than 6%. Using this information to produce a composition independent, average regular solution interaction parameter yields a value of 5.98 kcal/mole and a high critical temperature for phase separation of approximately 1250 °C. This suggests that the GaInN alloys are unstable over nearly the entire range of solid composition useful for photonic and electronic devices.

The molar free energy of mixing for $Ga_{1-x}In_xN$ can be approximated as[8]

$$\Delta G = \Omega x(1-x) + kT[x\ln(x) + (1-x)\ln(1-x)], \qquad (1)$$

where k is the Boltzman constant and Ω is the regular solution model interaction parameter. The first term on the right-hand side of Eq. (1) is the enthalpy of mixing given by the regular solution theory, i.e.,

$$\Delta H_M = \Omega x(1-x). \qquad (2)$$

The second term in Eq. (1) is the ideal configurational entropy of mixing based on the assumption of a random distribution of Ga and In atoms. The equilibrium InN solubility in GaN (the binodal point at a given temperature) is calculated as the composition where $\partial G/\partial x = 0$.[8] The spinodal composition is that where $\partial^2 G/\partial x^2 = 0$ at a given temperature.[8] The interaction parameter, Ω, is the only parameter in Eq. (1) that must be determined for the GaInN system.

The calculation of the enthalpy of mixing or the interaction parameter in III–V systems has been a topic of interest for nearly twenty-five years. In 1972 Stringfellow[9] developed the semi-empirical delta-lattice-parameter (DLP) model, which is found to yield surprisingly accurate interaction parameters for a wide range of III–V alloys knowing only the lattice constants of the binary constituents. In more recent years, the major component of this model, which always yields values of interaction parameter greater than or equal to zero, was determined to be the microscopic strain energy associated with the bond distortion in the alloy. The VFF model treats both the stretching and bending of the bonds[7] without adjustable parameters. In the case of a ternary alloy, $A_xB_{1-x}C$, the lattice is considered to be com-

a)Electronic mail: stringfellow@ee.utah.edu

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posed of five types of tetrahedra.[10] Each has a C atom at the center and the apexes are occupied by a combination of A and B atoms. The atoms on the mixed sublattice (A and B) are fixed at positions determined by the virtual-crystal approximation (VCA) while the atoms of the common element (C) are allowed to relax in each tetrahedron to minimize the total strain energy. The strain energy (E_m)can be written for each of the five tetrahedra as[7]

$$E_m = \frac{3}{8}\Sigma_{i=1}^{4}\alpha_i \frac{(d_i^2 - d_{i0}^2)^2}{d_{i0}^2} + \frac{6}{8}\Sigma_{i=1}^{4}\Sigma_{j=i+1}^{4}\frac{\beta_i+\beta_j}{2}\frac{(\mathbf{d}_i\cdot\mathbf{d}_j + d_{i0}d_{j0}/3)^2}{d_{i0}d_{j0}}, \quad (3)$$

where d_i is the distance between the center atom and a corner atom in the tetrahedron, while d_{i0} is the equilibrium length of this bond in the binary compound AC or BC. α and β, which can be obtained from the fitting of the elastic constants, are the bond stretching and the bond bending force constants, respectively. The mixing enthalpy is the summation of E_m over the five types of tetrahedra weighted by the distribution probabilityP_m,

$$\Delta H^M = \Sigma E_m P_m, \quad (4)$$

where the index m runs through all five tetrahedra. Note that ΔH^M, E_m, and P_m are all implicit functions of x. E_m and P_m are interdependent and must be solved simultaneously,[10] assuming a random distribution of A and B uncouples E_m and P_m and simplifies the calculation.[10]

Martins and Zunger[11] used the VFF model in the dilute limit ($x \ll 1$) to calculate the equilibrium bond lengths between the first nearest-neighbor atoms as well as the interaction parameters for several III–V alloys. They suggested the bond-bending energy of the VFF model be set to zero to compensate for errors caused by limiting the relaxation of the atoms to only one of the two sublattices. The interaction parameters calculated using this approximation agree well with the available experimental data for most III–V ternary alloys.

An alternative approach, used in the present work, is to allow the lattice to be fully relaxed up to the sixth nearest neighbor and to include both the bond-bending and bond-stretching energies. This approach is more physically reasonable; however, the calculation must be done numerically. Clearly, since the elastic parameters are typically significantly different for the two binary constituents, the value of Ω obtained from the regular solution enthalpy of mixing, Eq. (2), will be different for the two extremes of solid composition. In other words, the calculated interaction parameter will be composition dependent. In the present work, the solubility of InN in GaN and of GaN in InN were calculated independently and, not surprisingly, were found to be unequal at a given temperature. For calculation of the binodal and spinodal isotherms over the entire composition range and the critical temperature for the solid phase miscibility gap, a linearly averaged value, $[\Omega(x\sim 0)+\Omega(x\sim 1)]/2$, was used for simplicity. The input parameters for the VFF calculation are listed in Table I. Since the experimental data of the elastic constants is not available, α and β are extrapolated using the empirical equation suggested by Martin.[12] The crystal symmetry of both GaN and InN is taken to be cubic (zinc blende) even though the hexagonal (wurtzite) is more commonly observed in most III–V nitrides. Assuming that these two structures are different only in the atomic stacking sequence along the normal of their corresponding close-packed planes [(111) in zinc blende and (0001) for wurtzite) and the equilibrium bond lengths and force constants are the same, the resulting interaction parameters for the two structures are found to differ by only about 1%. Thus the two structures are considered equivalent in the strain energy calculations and the results presented here should closely approximate those for the wurtzite GaInN system.

TABLE I. Input parameters for the VFF calculation.

	α_0 (cubic)[a] (Å)	α[b] (N/m)	β[b] (N/m)
GaN	4.520	81.09	0.1500
InN	4.980	63.58	0.1266

[a]Reference 14.
[b]α and β are, respectively, the bond-stretching and bond-bending force constants defined in the VFF model. Since there are no experimental values available for GaN and InN, they are extrapolated following the work of Ref. 12.

Figure 1 shows calculated interaction parameters for both GaN-rich and InN-rich solids as a function of the number of neighbors relaxed. The values of Ω are seen to decrease significantly as the number of neighboring shells allowed to relax increases from 1 (equivalent to the VFF model) to approximately 4. For relaxation to the fifth and sixth nearest neighbors, the effect saturates. The slight increase in accuracy obtained by allowing relaxation to the fifth or sixth nearest neighbor is more than offset by the necessity to limit the calculation to very dilute alloys in order to prevent interactions between neighboring clusters. The limiting values of Ω are approximately 6.32 kcal/mole for the GaN-rich solid and 5.63 kcal/mole for the InN-rich solid. The average value, 5.98 kcal/mole, is about 38% smaller than the value of 9.60 kcal/mole calculated using the delta-lattice-parameter model.[13]

For the solid solubilities shown in Fig. 2, relaxation to

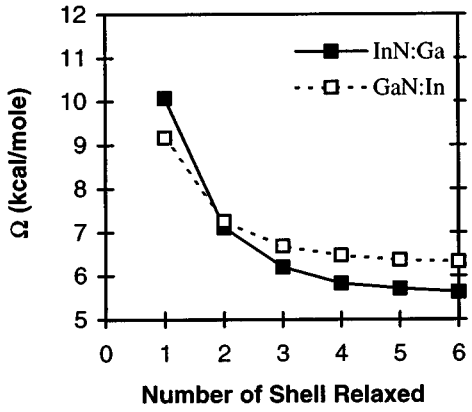

FIG. 1. Interaction parameters for the GaInN system vs the number of neighboring shells relaxed. The open squares represent calculated parameters for GaN-rich solutions and the closed squares are for InN-rich solutions. The lines simply connect the data points.

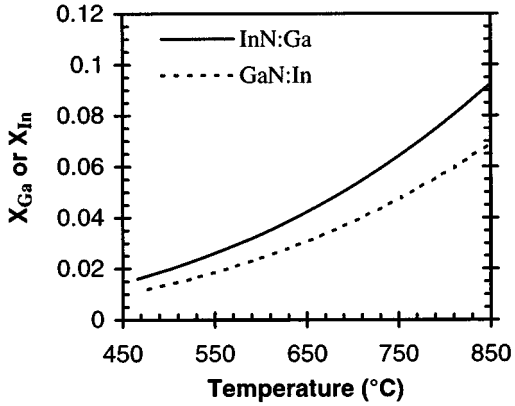

FIG. 2. Solubility of GaN in InN (InN:Ga) and InN in GaN (GaN:In) calculated using the VFF model with bond relaxation to the third nearest neighbor.

the third neighbor was used. This limits the range of solid composition for which the model is valid to approximately 7%, which is appropriate for the GaInN system, since the solubility is seen to be in the range of a few percent. In Fig. 3 the calculated binodal and spinodal compositions are shown versus temperature over the entire system using the average value of $\Omega = 5.98$ kcal/mode. The critical temperature is found to be near 1250 °C which exceeds the melting point of InN. At the maximum growth temperature used for

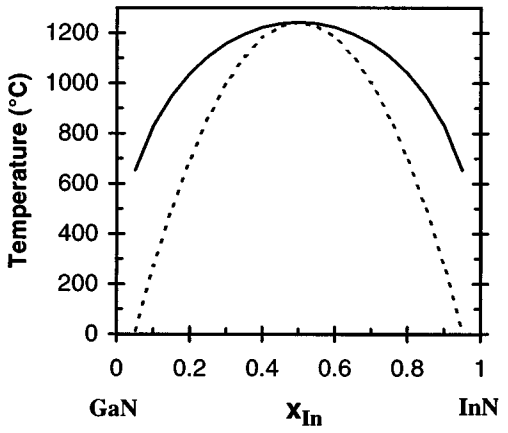

FIG. 3. Binodal (solid) and spinodal (dashed) curves for the $Ga_{1-x}In_xN$ system, calculated assuming a constant average value for the solid phase interaction parameter.

$Ga_{1-x}In_xN$ (800 °C), the InN solubility in GaN is calculated to be less than 6%.

The above results indicate that, in general, the $Ga_{1-x}In_xN$ alloys desirable for both photonic and electronic devices are unstable at the temperatures commonly used for epitaxial growth. This is supported by the results of annealing experiments performed by Osamura *et al.*[6] where phase separation in $Ga_{1-x}In_xN$ with $x \geqslant 0.1$. was observed after the samples were annealed in an argon ambient at 600 and 700 °C.

In summary, the solution thermodynamics for the $Ga_{1-x}In_xN$ system were explored by calculating the enthalpy of mixing using a modified VFF model where lattice relaxation to more distant neighbors is allowed. A large positive enthalpy of mixing is calculated. Using the ideal entropy of mixing, the binodal and spinodal curves for the GaInN system were calculated. At the maximum temperature typically used for the epitaxial growth of $Ga_{1-x}In_xN$ (800 °C), the solubility of InN is less than 6%. An average interaction parameter of 5.98 kcal/mole was calculated, yielding a critical temperature for phase separation of 1250 °C. These results indicate that $Ga_{1-x}In_xN$ alloys are unstable over most of the composition range at normal growth temperatures. This conclusion is supported qualitatively by the results of a published experimental investigation that reported the observation of phase separation in the GaInN system. The large region of solid immiscibility may explain the difficulty reported in the epitaxial growth of these alloys.

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